

ATTACHMENT 2

Addendum 1 - Risk Screening and Risk Management Recommendations for:
Veolia ES Technical Solutions, L.L.C.

Document 177

Addendum/Risk Screening and Risk Management Recommendations for: Veolia ES Technical Solutions, L.L.C., Sauget, Illinois - Explanation of Mercury Speciation, Dispersion and Methylation - w/CD attachment

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**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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ADDENDUM

**Risk Screening and Risk Management Recommendations for:
Veolia ES Technical Solutions, L.L.C.
Sauget, Illinois
(Formerly: "Onyx Environmental Services")**

Explanation of Mercury Speciation, Dispersion and Methylation

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Addendum

Risk Screening and Risk Management Recommendations for: Veolia ES Technical Solutions, L.L.C. Sauget, Illinois

I. Background

The "Risk Screening and Risk Management Recommendations for Veolia ES Technical Solutions, L.L.C., Sauget, Illinois," dated May 2007, (the "Veolia Risk Report") evaluated whether compliance by the Veolia facility with the emission standards for certain hazardous constituents established by 40 C.F.R. Part 63, Subpart EEE (the "Hazardous Waste Combustion – Maximum Achievable Control Technology Rule" or "HWC-MACT Rule") alone would be protective of human health. The Veolia Risk Report calculated the expected emissions of various hazardous constituents, including mercury, at the HWC-MACT Rule emissions standards for each incinerator stack at the Veolia facility. U.S. EPA conducted air dispersion and deposition modeling of these expected emissions from the Veolia facility (see *Dispersion Modeling of Incinerator Stack at Onyx Environmental Services*, dated June 15, 2006). Finally, U.S. EPA assessed the human health risks resulting from the modeled deposition of hazardous constituents from the Veolia facility. In conducting the site specific risk assessment for the Veolia Risk Report, USEPA followed the *Final Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities*, EPA 520-R-05-006, September 2005 ("HHRAP" or "risk assessment model").

Mercury deposition and runoff to water bodies results in the conversion of inorganic mercury to methylmercury within the water column. Methylmercury is of concern because it has a high potential for bioaccumulation and bioconcentration into aquatic species including fish. In other words, the emission and deposition of inorganic mercury may result in human exposure to methyl mercury through the food chain, i.e., fish. There is some indication of the potential for both recreational and subsistence fishing at the Frank Holten State Park lakes that are near the Veolia facility. Because of these site specific factors, the Veolia Risk Report considered the health risks posed by the conversion of inorganic mercury emitted by the Veolia facility into methyl mercury. Table 2 of the Veolia Risk Report provides the estimated the cancer risk and hazard quotients for various constituents including methyl mercury. The Veolia Risk Report concluded that emissions of mercury from the Veolia facility at the HWC-MACT Rule emissions standard would result in potential exposure to methyl mercury above U.S. EPA's risk management guidelines. Therefore, the Veolia Risk Report recommended that total annual stack emissions of mercury from the Veolia facility be limited to protect human health.

This Addendum explains how U.S. EPA calculated the conversion of expected emissions of inorganic mercury from the Veolia incinerator stacks to methylmercury for purposes of assessing potential human health risks in the Veolia Risk Report.

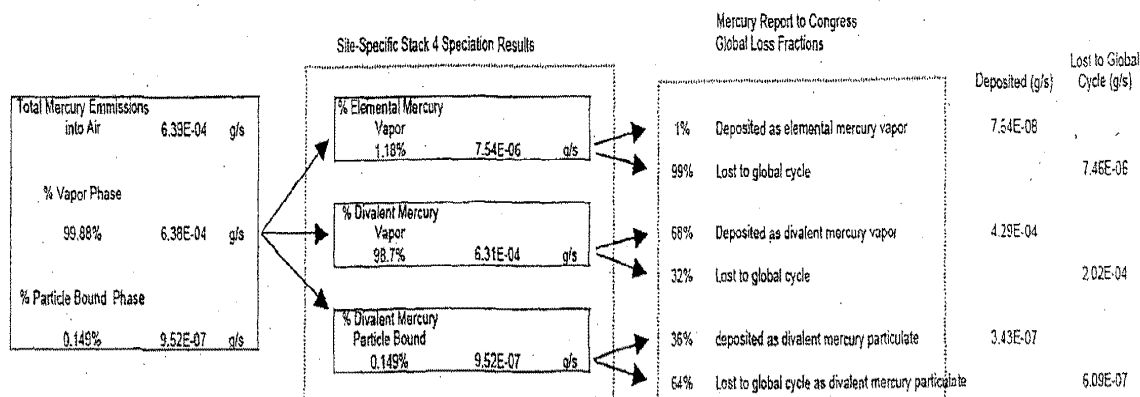
II. Speciation and Dispersion of Mercury Emissions

As described in the dispersion modeling report, emissions from Veolia's stacks were modeled as "unit" emissions wherein emission rates of the various phases (vapor, particulate, and particle-bound) are set to 1.0 gram per second. This methodology allows the modeler to use one set of modeling runs and scale the results by multiplying them by the actual or tested emission rate. After entering the constituent-specific emission rate, the risk assessment model (*Final Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities*, EPA 520-R-05-006, September 2005) further partitions the emissions to one or more of the phase-specific dispersion results. For example, an extremely volatile chemical may have the majority of its mass emitted assigned to the dispersion results of the modeled vapor phase. Similarly, a non-volatile pollutant like a heavy metal may be largely assigned to the dispersion results from the particle phase. These are important distinctions as the specific phases disperse and deposit on the surrounding area differently.

Mercury can be emitted not only in different phases (vapor and particle-bound) but in different species that also effect how mercury is dispersed and deposited. The primary species of concern are elemental mercury and divalent mercury. In March 2005, the Veolia facility conducted a stack test on only Stack 4 in order to measure the proportions of the various species and phases. U.S. EPA used the results of the Stack 4 test results for each incinerator stack in the risk assessment model in order to apportion the mercury emissions among the various phases and species.

The risk assessment model also accounts for the concept of "loss to global cycle" where some of the mercury is assumed to leave the study area without depositing. The fraction of a pollutant that remains in the vapor phase in the surrounding area is identified in the risk assessment model as F_v . This parameter tells the model how to partition the pollutant between the various phases. Since the "loss to global cycle" assumptions ultimately effect how the mercury species deposit, F_v must be individually calculated for the species of mercury and entered into the model. The following diagram shows the speciation of mercury from the stack test and the estimates for factoring "loss to global cycle" into the emission rates. The diagram also shows how F_v is calculated for both elemental and divalent mercury. Divalent mercury is modeled as mercuric chloride. The risk assessment model combines all of these factors to scale the results from the dispersion modeling and deposition results to site-specific air concentrations and deposition fluxes for the different species and phases of mercury. The risk assessment model used these scaled mercury concentrations as the source for further fate and transport modeling of mercury through the environment.

Figure 1. Phase Allocation and Speciation of Mercury for Veolia-Sauget Risk Assessment



Summary with Consideration of Loss to Global Cycle

Total mercury emitted deposited as divalent mercury

Deposited as divalent mercury vapor + Deposited as divalent mercury particulate
 = 4.29E-04 g/s
 or 67% of total mercury emitted

Total mercury deposited as elemental vapor

Deposited elemental mercury vapor = 7.54E-06 g/s
 0.0118% of total mercury emitted

	Total Deposited	Total Lost
Percent of Total	67%	33%

Vapor Fraction (Fv) of Deposited Mercury (for partitioning between vapor and particle bound deposition fluxes)

Fv (divalent mercury) = deposited as divalent mercury vapor / total divalent mercury deposited
 Fv (divalent mercury) = 0.998201425

Fv (elemental mercury) = deposited as elemental mercury vapor / total elemental mercury deposited
 Fv (elemental mercury) = 1

III. Mercury Fate, Transport and Methylation for the Veolia Risk Report

The following description of mercury dispersion and methylation is taken from the HHRAP and U.S. EPA's *Mercury Study Report to Congress*, EPA-452/R-97-003, December 1997 ("Mercury Report to Congress").

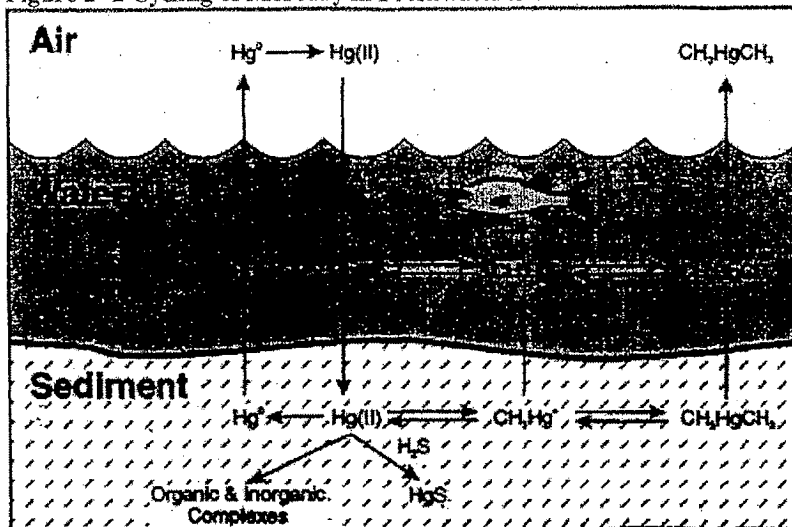
A. Fate and Transport of Mercury in the Environment

The movement and distribution of mercury in the environment can be confidently described only in general terms. There has been increasing consensus on many, but not all, of the detailed behaviors of mercury in the environment. The depiction of the mercury cycle in Figure 2-2 (from the Mercury Study Report to Congress) illustrates the major transfer and transformation processes expected to occur. These processes include a number of infinite and/or indefinite loops.

Mercury cycling and partitioning in the environment are complex phenomena that depend on numerous environmental parameters. The following points generally describe the key factors that affect the fate and transport of mercury in the environment.

- The form of mercury in air affects both the rate and mechanism by which it deposits to earth.
- Wet deposition apparently is the primary mechanism for transporting mercury from the atmosphere to surface waters and land.
- Once in aquatic systems, mercury can exist in dissolved or particulate forms and can undergo a number of chemical transformations (see Figure 2-2).
- Contaminated sediments at the bottom of surface waters can serve as an important mercury reservoir, with sediment-bound mercury recycling back into the aquatic ecosystem for decades or longer.
- Mercury has a long retention time in soils. As a result, mercury that has accumulated in soils may continue to be released to surface waters and other media for long periods of time, possibly hundreds of years.

Figure 2 -2 Cycling of Mercury in Freshwater Lake



Source: Adapted from Winfrey, M.R. and J.W.M. Rudd. 1990. Review -- Environmental Factors Affecting the Formation of Methylmercury in Low pH Lakes. *Environ. Toxicol. Chem.* 9:853-869.

B. Mercury Methylation and Bioaccumulation

Methylation of mercury is a key step in the entrance of mercury into food chains. The biotransformation of inorganic mercury species to methylated organic species in water bodies can occur in the sediment and the water column. Nearly 100% of the mercury that bioaccumulates in fish tissue is methylated.

Methylmercury production and accumulation in the freshwater ecosystem is an efficient process for accumulating mercury which can then be ingested by fish-eating (piscivores) birds, animals and people. In addition, methylmercury generally comprises a relatively greater percentage of the total mercury content at higher trophic levels. Accordingly, mercury exposure and accumulation is of particular concern for animals at the highest trophic levels in aquatic food webs and for animals and humans that feed on these organisms.

1. Calculating Mercury Concentrations in Surface Water and Sediments

HHRAP suggests these mechanisms in determining mercury loading of the water column:

- Direct deposition,
- Runoff from impervious surfaces within the watershed,
- Runoff from pervious surfaces within the watershed,
- Soil erosion over the total watershed,

- Direct diffusion of vapor phase mercury into the surface water, and
- Internal transformation of compounds chemically or biologically.

The total concentration of mercury is partitioned between the sediment and the water column. The HHRAP uses the Universal Soil Loss Equation (USLE) and a sediment delivery ratio to estimate the rate of soil erosion from the watershed. The equations recommended for estimating surface water concentrations include a sediment mass balance, in which the amount of sediment assumed to be buried and lost from the water body is equal to the difference between the amount of soil introduced to the water body by erosion and the amount of suspended solids lost in downstream flow. As a result, it is assumed that sediments do not accumulate in the water body over time, and equilibrium is maintained between the surficial layer of sediments and the water column. The total water column mercury concentration is the sum of the mercury concentration dissolved in water and the mercury concentration associated with suspended solids.

For the Veolia Risk Report, U.S. EPA used a computer software (IRAP™) that follows this methodology in calculating mercury concentrations in the water column. A copy of the IRAP™ archive for the Veolia Risk Report is attached in a compact disk. See Addendum Appendix A, IRAP™ Archive.

2. Methylation of Mercury

The net mercury methylation rate (the net result of methylation and demethylation) for most soils appears to be quite low; with much of the measured methylmercury in soils potentially resulting from wet deposition. Based on the information in Mercury Report to Congress, U.S. EPA assumes that 98 percent of the deposited mercury remains divalent mercury, and two percent speciates to organic mercury (methylmercury) in soil.

Both watershed erosion and direct atmospheric deposition can be important sources of mercury to a water body. In the absence of site-specific measurements to support evaluation of water body properties and biotic conditions relevant to mercury methylation, HHRAP generally recommends assuming that 85 percent of total mercury in surface water is divalent mercury, and the remaining mass is methylmercury.

Specifically, HHRAP recommends that a dissolved water concentration first be calculated for total mercury using the fate and transport parameters specified for mercuric chloride. Then, the dissolved total mercury concentration should be apportioned based on an 85 percent divalent and 15 percent methylmercury speciation split in the water body. HHRAP's Appendix B (Table B-4-24) presents the equations recommended for applying the speciation assumptions. The risk assessment software used by U.S. EPA for the Veolia Risk Report utilizes these equations consistent with the HHRAP.

3. Bioaccumulation of Methylmercury in Fish

After methylmercury is formed in the aquatic environment, the most significant concern for human health risk is uptake and bioaccumulation in fish. Bioaccumulation is the term

which refers to the finding that the concentration of mercury (in the form of methylmercury) in the aquatic environment increases as mercury moves up the food chain.

For methylmercury, U.S. EPA guidance recommends that the concentration in fish should be calculated using a methylmercury-specific Bioaccumulation Factor (BAF). The BAF is the ratio of the contaminant concentration in fish tissue to the contaminant concentration in the waterbody where the fish are exposed to the contaminant. The BAF accounts for uptake of contaminants into fish by a combination of several different mechanisms including water passing across the gills and consumption of sediments and dietary foods which could include plankton, daphnids, and other fish.

BAF values are based on dissolved water concentrations. U.S. EPA guidance recommends the following equation to calculate fish concentrations for chemicals which bioaccumulate including methylmercury (HHRAP):

$$C_{\text{fish}} = C_{\text{dw}} \times \text{BAF}_{\text{fish}}$$

Where

C_{fish}	=	Concentration of methylmercury in fish (mg/kg tissue)
C_{dw}	=	Dissolved phase water concentration (mg/Liter)
BAF_{fish}	=	Bioaccumulation factor for methylmercury (Liter/kg)

The dissolved phase water concentration (C_{dw}) is calculated as described above (Section B.2.). The recommended methylmercury BAF_{fish} value and the BAF value used in the Veolia Risk Report is 6.8E+06 (HHRAP Chemdat Database).

That BAF value is based on the geometric mean from measured BAF values obtained from a number of actual field studies of mercury bioaccumulation conducted at U.S. and Canadian lakes (Mercury Study Report). This value is considered to be appropriate for evaluating methylmercury uptake at other lakes and also accounts for uptake into fish at a high trophic level (i.e., trophic level 4 - fish at the highest end of the food chain). The available information indicates that the lakes at Frank Holten State Park contain fish at trophic level 4.

4. Fish Consumption Rate

During the 2003 public comment period, the public raised the concern that U.S. EPA had not considered subsistence fishing at the Frank Holten State Park lakes. In addition, reports of subsistence fishing were provided to U.S. EPA. Visits to the lakes by U.S. EPA indicated the potential for recreational and subsistence fishing there. Frank Holten State Park lakes have naturally occurring fish and are stocked annually with game fish. In addition, U.S. EPA has concluded that the area surrounding the Veolia facility is a potential environmental justice community. For these reasons, U.S. EPA used Adult and Child Fisher exposure scenarios recommended by HHRAP for assessing potential risks posed by methylmercury in fish.

The risk assessment computer software used by U.S. EPA, IRAP™, used the default consumption rates in Appendix C, Table C-1-4 of the HHRAP, which are derived from the 1987-1988 USDA National Food Consumption Survey. Table C-1-4 of the HHRAP, Appendix C, states that these default consumption rates may be used to assess exposure to contaminants in foods grown, raised, or caught at a specific site. It is important to note that these default consumption rates are not intended to specifically represent subsistence fishers or other high-end consumers of home-caught fish. The default consumption rates are derived from data that represent the average amount of fish eaten by people who fish in a local water body and eat at least some of the fish they catch. Since there is no reliable site-specific information available about the amount of fish consumed from Frank Holten State Park lakes, the Veolia Risk Report used the recommended default consumption rate values shown in the HHRAP. These consumption rates convert to 87.5 grams per day for an Adult Fisher and 13.2 grams per day for a Child Fisher. These are the values used in the calculations below.

5. Calculation of Methylmercury Hazards

U.S. EPA calculated the hazard quotients for methylmercury appearing in Table 2 of the Veolia Risk Report according to the following equations:

Calculation of methylmercury concentration in fish

$$C_{\text{fish}} = C_{\text{dw}} \times \text{BAF}_{\text{fish}}$$

Where,

C_{fish} = Concentration of methylmercury in fish (mg/kg FW tissue)

C_{dw} = Methylmercury dissolved phase water concentration (mg/L)

BAF_{fish} = Bioaccumulation factor for methylmercury in fish (L/kg FW tissue)

Calculation of Average Daily Dose of Methylmercury from Fish

$$\text{ADD} = (C_{\text{fish}} \times \text{CR}_{\text{fish}} \times \text{EF} \times \text{ED}) / (\text{BW} \times \text{AT} \times 365 \text{ days/year} \times 1000 \text{ g/kg})$$

Where,

ADD = Average Daily Dose—the amount of methylmercury at the exchange boundary (mg/kg/day)

C_{fish} = methylmercury concentration in fish (mg/kg)

CR_{fish} = Consumption rate—the amount of contaminated fish consumed per day (g/day)

EF = Exposure Frequency (days/year)

ED = Exposure Duration (30 years)

BW = Average Body Weight of the Receptor over the Exposure Period (kg)

AT = Averaging Time (30 years)

Calculation of Methylmercury Hazard Quotient

$$HQ = ADD/RfD$$

Where,

HQ= Hazard Quotient (unitless)

ADD = Average Daily Dose (mg/kg-day)

RfD = Reference Dose (mg/kg-day)

Calculation of Adult Fisher Scenario Total Hazard Quotient¹

$$C_{fish} = C_{dw} \times BAF_{fish}$$

Where,

$$\text{Stack 2 } C_{dw} = 6.16E-9 \text{ mg/L}^2$$

$$\text{Stack 3 } C_{dw} = 6.09E-9 \text{ mg/L}$$

$$\text{Stack 4 } C_{dw} = 1.52E-8 \text{ mg/L}$$

$$BAF_{fish} = 6,800,000 \text{ L/kg}$$

$$\text{Stack 2 } C_{fish} = 0.0419 \text{ mg/kg}$$

$$\text{Stack 3 } C_{fish} = 0.0414 \text{ mg/kg}$$

$$\text{Stack 4 } C_{fish} = 0.103 \text{ mg/kg}$$

And,

$$ADD = (C_{fish} \times CR_{fish} \times EF \times ED) / (BW \times AT \times 365 \text{ days/year} \times 1000 \text{ g/kg})$$

Where,

$$CR_{fish} = 87.5 \text{ g/day (from HHRAP)}$$

$$EF = 350 \text{ days/year (from HHRAP)}$$

$$ED = 30 \text{ years (from HHRAP)}$$

$$BW = 70 \text{ kg (from HHRAP)}$$

$$AT = 30 \text{ years (from HHRAP)}$$

$$\text{Stack 2 } ADD = 0.000050 \text{ mg/kg-day}$$

¹ The values used here have been rounded for brevity. Therefore, these calculations differ slightly from those in Table 2 of the Veolia Risk Report due to this rounding.

² The specific values for the contributing concentration of methylmercury for each stack in this calculation are taken from the IRAPTM run generated for the Veolia Risk Report. See Addendum Appendix B, Reprint of Select IRAPTM Reports, Media Concentrations.

Stack 3 ADD = 0.000050 mg/kg-day

Stack 4 ADD = 0.000123 mg/kg-day

Therefore,

$$HQ = ADD/RfD$$

Where,

RfD = 0.0001 mg/kg-day

Stack 2 HQ = 0.50

Stack 3 HQ = 0.50

Stack 4 HQ = 1.23

Total Adult Fisher methylmercury HQ = 2.23

Calculation of Child Fisher Scenario Total Hazard Quotient³

$$C_{fish} = C_{dw} \times BAF_{fish}$$

Where,

Stack 2 $C_{dw} = 6.16E-9$ mg/L⁴

Stack 3 $C_{dw} = 6.09E-9$ mg/L

Stack 4 $C_{dw} = 1.52E-8$ mg/L

$BAF_{fish} = 6,800,000$ L/kg

Stack 2 $C_{fish} = 0.0419$ mg/kg

Stack 3 $C_{fish} = 0.0414$ mg/kg

Stack 4 $C_{fish} = 0.103$ mg/kg

And,

$$ADD = (C_{fish} \times CR_{fish} \times EF \times ED) / (BW \times AT \times 365 \text{ days/year} \times 1000 \text{ g/kg})$$

Where,

$CR_{fish} = 13.2$ g/day (from HHRAP)

EF = 350 days/year (from HHRAP)

ED = 6 years (from HHRAP)

BW = 15 kg (from HHRAP)

AT = 6 years (from HHRAP)

³ The values used here have been rounded for brevity. Therefore, these calculations differ slightly from those in Table 2 of the Veolia Risk Report due to this rounding.

⁴ The specific values for the contributing concentration of methylmercury for each stack in this calculation are taken from the IRAPTM run generated for the Veolia Risk Report. See Addendum Appendix B, Reprint of Select IRAPTM Reports, Media Concentrations.

Stack 2 ADD = 0.000035 mg/kg-day

Stack 3 ADD = 0.000035 mg/kg-day

Stack 4 ADD = 0.000087 mg/kg-day

Therefore,

$HQ = ADD/RfD$

Where,

$RfD = 0.0001 \text{ mg/kg-day}$

Stack 2 HQ = 0.35

Stack 3 HQ = 0.35

Stack 4 HQ = 0.87

Total Child Fisher methylmercury HQ = 1.57